

Link between isoprene and secondary organic aerosol (SOA): Pyruvic acid oxidation yields low volatility organic acids in clouds

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Received 5 December 2005; revised 19 January 2006; accepted 17 February 2006; published 29 March 2006.

[1] Aqueous-phase oxidation (in clouds and aerosols) is a potentially important source of organic aerosol and could explain the atmospheric presence of oxalic acid. Methylglyoxal, a water-soluble product of isoprene, oxidizes further in the aqueous phase to pyruvic acid. Discrepancies in the literature regarding the aqueous-phase oxidation of pyruvic acid create large uncertainties in the in-cloud yields of secondary organic aerosol (SOA) and oxalic acid. Resolving the fate of aqueous-phase pyruvic acid is critical to understanding SOA formation through cloud processing of water-soluble products of isoprene, other alkenes and aromatics. In this work, aqueous-phase photochemical reactions of pyruvic acid and hydrogen peroxide at pH values typical of clouds were conducted and demonstrated that photochemical oxidation of pyruvic acid yields glyoxylic, oxalic, acetic and formic acids. Oxalic and glyoxylic acids remain mostly in the particle phase upon droplet evaporation. Thus isoprene is an important precursor of in-cloud SOA formation. **Citation:** Carlton, A. G., B. J. Turpin, H.-J. Lim, K. E. Altieri, and S. Seitzinger (2006), Link between isoprene and secondary organic aerosol (SOA): Pyruvic acid oxidation yields low volatility organic acids in clouds, *Geophys. Res. Lett.*, 33, L06822, doi:10.1029/2005GL025374.

1. Introduction

[2] Secondary (atmospheric) formation via cloud processing is well documented for sulfate and has been hypothesized for organic particulate matter (PM) [Blando and Turpin, 2000]. Recent modeling investigations conducted by Ervens *et al.* [2004] and Lim *et al.* [2005] suggest that aqueous phase reactions of water-soluble organics (i.e., glyoxal, methylglyoxal, and glycolaldehyde) can yield secondary organic aerosol (SOA) through formation of carboxylic acids (e.g., glyoxylic, glycolic, and oxalic acids) and subsequent cloud droplet evaporation. In-cloud production of oxalic acid from the gas-phase precursors ethene and acetylene has also been proposed [Warneck, 2003]. Elevated concentrations of organic aerosol have been measured in the free tropo-

sphere and cannot be reproduced by models including primary emissions and homogeneous secondary formation [Heald *et al.*, 2005].

[3] Oxalic acid is the most abundant atmospheric particulate organic diacid [Kawamura and Yasui, 2005; Mochida *et al.*, 2003; Kawamura *et al.*, 1996]. The temporal dynamics (seasonal and diurnal variations) of oxalic acid suggest that its abundance is predominantly due to secondary formation [Rogge *et al.*, 1993; Kawamura *et al.*, 1996]. In-cloud and below cloud measurements [Crahan *et al.*, 2004], in addition to other field measurements [Yu *et al.*, 2005], support an in-cloud formation mechanism for oxalic acid.

[4] In Lim's proposed mechanism [Lim *et al.*, 2005], isoprene is oxidized to glycolaldehyde, glyoxal and methylglyoxal in the gas phase. These compounds are highly water soluble [Berterton and Hoffmann, 1988] and partition into cloud droplets where they are oxidized further by OH to form low volatility organic acids (glyoxylic and oxalic acids). Upon cloud evaporation these organics remain mostly (i.e., 75% and 90%, respectively) in the particle phase [Limbeck *et al.*, 2003], forming SOA. The key difference between the chemistry used in the Lim and Ervens models is the aqueous-phase fate of pyruvic acid. Pyruvic acid ($H_{\text{eff}} = 3.1 \times 10^5 \text{ M atm}^{-1}$, [Staudinger and Roberts, 1996]) is the main aqueous-phase oxidation product of methylglyoxal, a well-known isoprene [Talbot *et al.*, 1995] and aromatic [Andino *et al.*, 1996] oxidation product. The importance of the methylglyoxal - pyruvic acid pathway is illustrated by the observation that the gas-phase oxidation of isoprene yields 4.5 times more methylglyoxal than glyoxal [Spaulding *et al.*, 2003]. In the mixed-phase atmospheric model of Ervens *et al.* [2004], pyruvic acid is converted to acetaldehyde and therefore the methylglyoxal - pyruvic acid pathway does not yield SOA. This pathway is quite important to determining the yields of organic acids and SOA from cloud processing of compounds like toluene and isoprene.

[5] In this paper we present an investigation of the aqueous-phase photochemistry and fate of pyruvic acid, and discuss implications for SOA formation through cloud processing. A companion paper identifies the formation of oligomers in these controlled experiments (K. E. Altieri *et al.*, Formation of oligomers in cloud-processing: Reactions of isoprene oxidation products, submitted to *Environmental Science and Technology*, 2005, hereinafter referred to as Altieri *et al.*, submitted manuscript, 2005). Resolving the discrepancy in the literature regarding the fate of aqueous phase pyruvic acid is needed in order to determine the global importance of isoprene and other methylglyoxal

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Table 1. Experimental Conditions and Controls^a

Initial Conditions	Experiment 1, N = 2, PA+UV+H ₂ O ₂	Experiment 2, N = 1, PA+UV+H ₂ O ₂
PA concentration, °C, pH	10 mM, 25, 2.7	5 mM, 25, 3.1
UV control	PA + H ₂ O ₂	PA + H ₂ O ₂
H ₂ O ₂ control	PA + UV	PA + UV

^aPA = Pyruvic Acid; initial H₂O₂ concentration is twice the initial pyruvic acid concentration. Typical cloud/fog pH = 2–5.

sources (e.g., other alkenes and aromatics) to SOA formation through cloud processing.

2. Methods and Materials

2.1. Experimental Reactions

[6] Batch photochemical aqueous reactions of pyruvic acid and hydrogen peroxide were conducted in 1 L borosilicate vessels (Table 1). The UV source was a low-pressure monochromatic (254 nm) mercury lamp in a quartz immersion well. The lamp was warmed up for 45 minutes prior to the beginning of the experiments. The reaction vessels were placed on magnetic stirrers and wrapped in aluminum foil to minimize the influence of ambient UV radiation. Solutions were prepared in 1 L volumetric flasks and then poured into the reaction vessels. For each experiment (N = 3) there were two control experiments: 1) an UV control (pyruvic acid and H₂O₂ without UV) and 2) an H₂O₂ control (pyruvic acid and UV without H₂O₂). Additionally, H₂O₂ was exposed to UV in the absence of organics (N = 2); these experiments were used to determine organic acid method detection limits (MDL). Further details are provided in the auxiliary material¹.

[7] Samples were taken in the reaction vessel initially, at 5 minutes, and then every 20–30 minutes over 3 hours, with 10% of samples collected in duplicate. Each pyruvic acid experiment generated approximately 30 samples. Hydrogen peroxide in the samples was destroyed with 0.5% catalase aqueous solution (0.25 μL/1 mL of sample) immediately [Stefan *et al.*, 1996]. The sample vials were then capped, shaken briefly, and stored in the freezer in the dark until analysis. Reaction vessel solutions were initially supersaturated with oxygen and at the end of the experiment oxygen levels had dropped to 2–3% of their saturated values, presumably due to oxygen consumption during oxidation reactions (Table S1). Cloud droplets are saturated with oxygen. Previous organic photochemical batch experiments conducted with and without replacement of oxygen have demonstrated that oxygen levels in solution affect reaction rates but not products [Leitner and Dore, 1997].

2.2. Analytical Procedures

[8] All standards and samples were analyzed in triplicate for carboxylic acids by high performance liquid chromatography (HPLC) with UV absorbance detection, and by an electrospray ionization/mass spectrometer (ESI/MS) consisting of an autosampler and quadrupole mass-selective detector equipped with an atmospheric pressure electrospray ionization source. The mean absorbance (±1 standard deviation)

of each triplicate analysis was reported and used for quantization (see auxiliary material).

2.3. Quality Control

[9] Recoveries for carboxylic acids were calculated by filling the reaction vessels with standard solutions that were “sampled” as during an experiment. Recoveries for pyruvic, acetic, formic and oxalic acid were 93%, 100%, 80% and 100%, respectively. Precision for carboxylic acids was 9%, expressed as a coefficient of variation of duplicate samples (N = 7). Oxalic acid concentrations in samples analyzed independently by HPLC and ESI/MS agreed within ±0.06 mM and were not significantly different based on a two-sided t-test (p = 0.05). Method detection limits for oxalic, glyoxylic, pyruvic, acetic, and formic acids were 0.04, 0.02, 0.41, 0.44 and 0.44 mM, respectively, calculated as three times the standard deviation of concentrations measured in the “organic control” (i.e., H₂O₂ and UV) samples. Analysis of independent standards confirmed that measurement accuracy was within 10%. Data analyses presented below use carboxylic acid concentrations determined by HPLC, except that ESI/MS measurements of glyoxylic acid concentrations were used because they had better precision.

3. Results

[10] Carboxylic acid concentration time profiles were similar for each experiment and show that substantial oxalic acid is produced during the photochemical oxidation of pyruvic acid in aqueous solution, consistent with the mechanism proposed by Lim *et al.* [2005]. A simplified oxidation scheme is presented in Figure 1; the associated reactions are listed in Table S1.

[11] Oxalic acid production is shown in Figure 2. Experiments show substantial oxalic acid production while the controls do not. (Oxalic acid concentrations were below detection limits in all Experiment 2 and 3 controls, controls from preliminary experiments and controls from subsequent experiments involving pyruvic acid conducted in our laboratory. The two Experiment 1 controls above detection limits are anomalous.) These results suggest that oxalic acid is produced by •OH oxidation of precursors. The oxalic acid production of Experiment 1 was approximately twice the production of Experiment 2, reflecting the factor of two difference in the initial pyruvic acid concentrations.

[12] A concentration time profile is shown in Figure 3. Time profiles for controls (Figure S1) are discussed in the

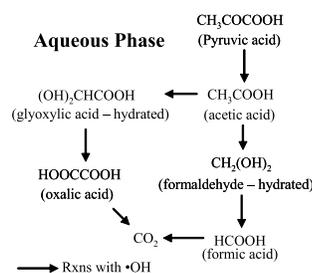


Figure 1. Pyruvic acid oxidation; detailed reactions given in Table S1. Pyruvic acid also reacts directly with H₂O₂ to form acetic acid. The atmospheric importance of this reaction remains to be determined. Pyruvic acid pKa = 2.93; acids exist in equilibrium with disassociated forms.

¹Auxiliary material is available at <ftp://ftp.agu.org/apend/g/2005g1025374>.

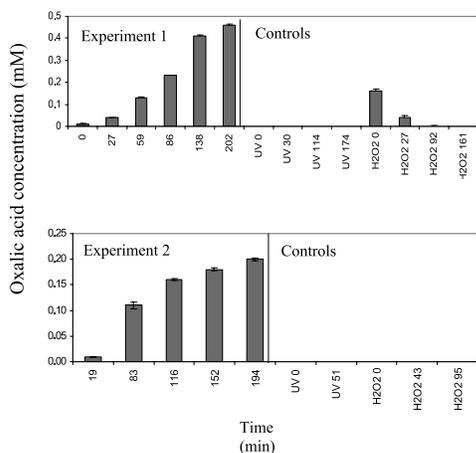


Figure 2. Oxalic acid concentrations (mM). Controls are “UV” (for pyruvic acid + H₂O₂) and “H₂O₂” (for pyruvic acid + UV) followed by the collection time.

auxiliary material. Rapid pyruvic acid loss occurs initially due to reaction with H₂O₂, before the solution can be transferred to the reaction vessel where H₂O₂ is photolyzed to •OH. The pyruvic acid concentration does not drop to zero, but asymptotically approaches 1 mM although the detection limit is 0.4 mM. We suspect this is due to oligomer formation, of which pyruvic acid is a component monomer (Altieri et al., submitted manuscript, 2005). HPLC analysis breaks down oligomers to their monomeric components. Acetic acid production occurs regardless of the initial oxidant, H₂O₂ or •OH. The predicted pyruvic acid concentration, calculated from the loss rate measured by Stefan and Bolton [1999] for oxidation of pyruvic acid with hydrogen peroxide in the absence of UV, is shown in Figure 3 in order to illustrate pyruvic acid degradation prior to transfer of the solution into the reaction vessel. The gray bar in the graph represents the time taken to transfer the solution to the reaction vessel, measure the solution pH and dissolved oxygen (DO), and take the first sample. The difference in time between the introduction of hydrogen peroxide into the volumetric flask and collection of the first sample was approximately 15 minutes. The pyruvic acid data points to the left of the gray bar were taken directly from the volumetric flask during a subsequent experiment with a solution identical to that of Experiment 1. These pyruvic acid concentrations are not significantly different from those predicted and reconcile the loss of pyruvic acid prior to the first experimental sample. In the reaction vessel H₂O₂ is converted to •OH. Hydroxyl radical then reacts with pyruvic acid and its product, acetic acid, initiating formation of oxalic and glyoxylic acids. Note pyruvic acid is oxidized to acetic acid by H₂O₂ or •OH, but subsequent production of oxalic and glyoxylic acid does not begin until •OH is formed. When H₂O₂ is the only oxidant present (no •OH) glyoxylic and oxalic acids do not form (Figure S1a). Note that glyoxylic acid production precedes oxalic acid production, as predicted in the Lim mechanism.

4. Discussion

[13] These results verify that aqueous-phase photochemical oxidation of pyruvic acid yields low volatility organic

acids, including glyoxylic and oxalic acids as proposed in the Lim model. These acids will remain predominantly in the particle phase upon droplet evaporation. The yield of oxalic acid from reacted pyruvic acid at laboratory conditions (25°C; reduced oxygen compared to clouds) is 0.06 on a molar basis. With the best available kinetic data and realistic tropical cloud conditions, Lim et al. [2005] predict that 50 ng/m³ of organic acids will form in the Amazon and 1.6 Tg/yr of SOA will form globally from isoprene alone through this mechanism. (Global biogenic SOA is roughly 8–40 Tg/yr [IPCC, 2001].) Many compounds besides isoprene also form methylglyoxal and subsequently pyruvic acid and therefore contribute to in-cloud SOA formation through this pathway. In addition, similar reactions could occur in the aqueous phase of atmospheric particles. Aqueous-phase oligomer formation (described by Altieri et al. (submitted manuscript, 2005)) is expected to drive additional organic acid formation (i.e., by enhancing the effective Henry’s Law constants of precursor carbonyls) and to reduce the vapor pressure of products, further enhancing SOA formation. Therefore, because aqueous-phase pyruvic acid oxidation yields low volatility acids, isoprene is an important precursor of SOA and in-cloud formation could be a substantial contributor to SOA concentrations regionally and globally, particularly in the free troposphere.

[14] This paper also adds to the growing body of evidence linking the atmospheric presence of oxalic acid to in-cloud formation [Yu et al., 2005; Crahan et al., 2004; Chebbi and Carlier, 1996]. Lim et al. [2005] and Ervens et al. [2004] predict 1–200 ng m⁻³ of oxalic acid and 50–300 ng m⁻³ of low volatility acids after 1–3 days of intermittent cloud processing. This is 10–25% of measured oxalic acid concentrations, which are on the order of 10–800 ng m⁻³ [Baboukas et al., 2000; Kawamura and Yasui, 2005]. These are likely to be under-predictions for a number of reasons discussed above. Therefore, it is quite plausible that in-cloud and aerosol-phase aqueous reactions could explain the atmospheric presence of oxalic acid.

[15] Incorporation of in-cloud SOA formation into regional and global models might explain the “missing

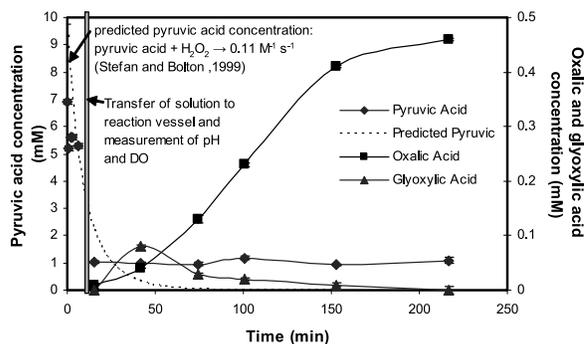


Figure 3. Time profile for pyruvic acid oxidation. Pyruvic acid and oxalic acids by HPLC and glyoxylic acid by ESI/MS. The predicted loss of pyruvic acid by H₂O₂ in the absence of other scavengers is shown by the dashed line. Measurements before the gray bar were taken directly from the volumetric flask. Time = 0 is the time at which H₂O₂ was placed in the volumetric flask. The solution was poured into the reaction vessel (UV) and first sample was taken about 15 minutes later.

source" identified by *Heald et al.* [2005] and is needed to improve prediction of the concentration, size and behavior of atmospheric aerosols for the effective resolution of issues associated with PM and health, visibility and climate.

[16] **Acknowledgments.** The authors gratefully acknowledge the helpful discussions with Barbara Ervens and Adam Reff. This research was supported by the U.S. EPA Science to Achieve Results (STAR) program (R831073) and an Air & Waste Management Association Air Pollution Research Grant (APERG). Although the research described in this paper has been funded by the U.S. EPA, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the EPA; no official endorsement should be inferred.

References

- Andino, J. M., J. N. Smith, R. C. Flagan, W. A. Goddard III, and J. H. Seinfeld (1996), Mechanism of atmospheric photooxidation of aromatics: A theoretical study, *J. Phys. Chem.*, *100*, 10,967–10,980.
- Baboukas, E. D., M. Kanakidou, and N. Mihalopoulos (2000), Carboxylic acids in gas and particulate phase above the Atlantic Ocean, *J. Geophys. Res.*, *105*, 14,459–14,472.
- Betterton, E. A., and M. R. Hoffmann (1988), Henry's law constants of some environmentally important aldehydes, *Environ. Sci. Technol.*, *22*, 1415–1418.
- Blando, J. D., and B. J. Turpin (2000), Secondary organic aerosol formation in cloud and fog droplets: A literature evaluation of plausibility, *Atmos. Environ.*, *34*, 1623–1632.
- Chebbi, A., and P. Carlier (1996), Carboxylic acids in the troposphere, occurrence, sources and sinks: A review, *Atmos. Environ.*, *30*, 4233–4249.
- Crahan, K. K., D. Hegg, D. S. Covert, and H. Jonsson (2004), An exploration of aqueous oxalic acid production in the coastal marine atmosphere, *Atmos. Environ.*, *23*, 3757–3764.
- Ervens, B., G. Feingold, G. J. Frost, and S. M. Kreidenweis (2004), A modeling study of aqueous production of dicarboxylic acids: 1. Chemical pathways and speciated organic mass production, *J. Geophys. Res.*, *109*, D15205, doi:10.1029/2003JD004387.
- Heald, C. L., D. J. Jacob, R. J. Park, L. M. Russell, B. J. Huebert, J. H. Seinfeld, H. Liao, and R. J. Weber (2005), A large organic aerosol source in the free troposphere missing from current models, *Geophys. Res. Lett.*, *32*, L18809, doi:10.1029/2005GL023831.
- Intergovernmental Panel on Climate Change (2001), *Climate Change 2001: The Scientific Basis*, edited by J. T. Houghton et al., Cambridge University Press, New York.
- Kawamura, K., and O. Yasui (2005), Diurnal changes in the distribution of dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban Tokyo atmosphere, *Atmos. Environ.*, *39*, 1945–1960, doi:10.1016/j.atmosenv.2004.12.014.
- Kawamura, K., H. Kasukabe, and L. Barrie (1996), Source and reaction pathways of dicarboxylic acids, ketoacids, and dicarbonyls in Arctic aerosols: One year of observations, *Atmos. Environ.*, *30*, 1709–1722.
- Leitner, N. K. V., and M. Dore (1997), Mechanism of the reaction between hydroxyl radicals and glycolic, glyoxilic, acetic, and oxalic acids in aqueous solution: Consequence on hydrogen peroxide consumption in the H₂O₂/UV and O₂/H₂O₂ systems (in French), *Water Res.*, *6*, 1383–1397.
- Lim, H.-J., A. G. Carlton, and B. J. Turpin (2005), Isoprene forms secondary organic aerosol through cloud processing: Model simulations, *Environ. Sci. Technol.*, *39*, 4441–4446.
- Limbeck, A., M. Kulmala, and H. Puxbaum (2003), Secondary organic aerosol formation in the atmosphere via heterogeneous reaction of gaseous isoprene on acidic particles, *Geophys. Res. Lett.*, *30*(19), 1996, doi:10.1029/2003GL017738.
- Mochida, M., N. Umemoto, K. Kawamura, and M. Uematsu (2003), Bimodal size distribution of C₂–C₄ dicarboxylic acids in the marine aerosols, *Geophys. Res. Lett.*, *30*(13), 1672, doi:10.1029/2003GL017451.
- Rogge, W. F., M. A. Mazurek, L. M. Hildemann, and G. R. Cass (1993), Quantification of urban organic aerosols at a molecular level: Identification, abundance and seasonal variation, *Atmos. Environ.*, *27*, 1309–1330.
- Spaulding, R. S., G. W. Schade, A. H. Goldstein, and M. J. Charles (2003), Characterization of secondary atmospheric photooxidation products: Evidence for biogenic and anthropogenic sources, *J. Geophys. Res.*, *108*(D8), 4247, doi:10.1029/2002JD002478.
- Staudinger, J., and P. V. Roberts (1996), A critical review of Henry's law constants for environmental applications, *Crit. Rev. Environ. Sci. Technol.*, *26*, 205–297.
- Stefan, M. I., and J. R. Bolton (1999), Reinvestigation of the acetone degradation mechanism in dilute aqueous solution by the UV/H₂O₂ process, *Environ. Sci. Technol.*, *30*, 870–873.
- Stefan, M. I., A. R. Hoy, and J. R. Bolton (1996), Kinetics and mechanism of the degradation and mineralization of acetone in dilute aqueous solution sensitized by the UV photolysis of hydrogen peroxide, *Environ. Sci. Technol.*, *30*, 2382–2390.
- Talbot, R. W., B. W. Mosher, B. G. Heikes, D. J. Jacob, J. W. Munger, B. C. Daube, W. C. Keene, J. R. Maben, and R. S. Artz (1995), Carboxylic acids in the rural continental atmosphere over the eastern United States during the Shenandoah Cloud and Photochemistry Experiment, *J. Geophys. Res.*, *100*, 9335–9344.
- Warneck, P. (2003), In-cloud chemistry opens pathway to the formation of oxalic acid in the marine atmosphere, *Atmos. Environ.*, *37*, 2423–2427.
- Yu, J. Z., X.-F. Huang, J. Xu, and M. Hu (2005), When aerosol sulfate goes up, so does oxalate: Implication for the formation mechanisms of oxalate, *Environ. Sci. Technol.*, *29*, 128–133.

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